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## Synthesis and Spectral Properties of 3,3'-Bis(dipyrrolylmethene)

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Abstract—Bis(2,4,7,8,9-pentamethyldipyrrolylmethene-3-yl)(4'-methoxyphenyl)methane dihydrobromide was synthesized and its spectral properties were studied. It was found that the basicity of the ligand 3,3'-bis-(dipyrrolylmethene) decreases upon insertion of the methoxyphenyl group in the 3,3'-spacer.

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To study the influence of the central spacer nature on spectral properties of alkylated 3,3'-bis(dipyrrolylmethenes), we have synthesized bis(2,4,7,8,9-pentamethyldipyrrolylmethene-3-yl)(4'-methoxyphenyl)methane dihydrobromide (H<sub>2</sub>L·2HBr) in which, as differentiated from the ligands synthesized earlier [1, 2], one of hydrogen atoms in the 3,3'-spacer is replaced by a methoxyphenyl group. The compound was identified and characterized by the <sup>1</sup>H NMR, IR, and electron spectroscopy, and elemental analysis methods. The synthesis of bis(2,4,7,8,9-pentamethyldipyrrolylmethene-3-yl)(4'-methoxyphenyl)methane dihydrobromide (III) was carried out according to the scheme bellow.

The previous studies [1, 2] have shown that the increase in the degree of alkylating pyrrole nuclei of 3,3'-bis(dipyrrolylmethene) molecules results in a significant amplification of the basicity of nitrogen atoms of (>N and >N-H) coordination centers and to increase in the stability of coordination compounds





**Fig. 1.** Electronic absorption spectra of bis(2,4,7,8,9-pentamethyldipyrrolylmethene-3-yl)(4'-methoxyphenyl)methane solutions: (a) in C<sub>6</sub>H<sub>6</sub> (c 7.1×10<sup>-6</sup> M); (b) in DMF (c 1.8×10<sup>-4</sup> M, H<sub>2</sub>L·2HBr, c 8.9×10<sup>-6</sup> M, H<sub>2</sub>L); (*I*) H<sub>2</sub>L and (*2*) H<sub>2</sub>L·2HBr.

with d-metals. According to the published data [3], the CH<sub>3</sub>O group in anisol exhibits positive mesomeric and negative inductive effects. The aim of this work was to estimate the effect of the methoxyphenyl substituent in the central spacer on practically significant physicochemical properties of the ligand.

Comparison of the spectral data for dihydrobromides of the synthesized ligand and of bis(2,4,7,8,9pentamethyldipyrrolylmethene-3-yl)methane, the ligand with a similar type of alkylation of pyrrole fragments shows that the insertion of the methoxyphenyl group into the 3,3'-spacer results in a low-frequency (by 26 cm<sup>-1</sup>) shift of the band of stretching vibrations of N–H bonds in the IR spectrum, a small down field shift of the signals of protons of NH-groups in the <sup>1</sup>H NMR spectrum [2], and a bathochromic shift (up to 8 nm) of the maximum of the long-wave band in the electron absorption spectra of solutions in organic solvents.

The hydrobromide salt of bis(2,4,7,8,9-pentamethyldipyrrolylmethene-3-yl)(4'-methoxyphenyl)methane is stable in inert (C<sub>6</sub>H<sub>6</sub>) and proton-donor(CHCl<sub>3</sub>) solvents (see Fig. 1a). Quantitative characteristics of electron absorption spectra of corresponding solutions remain unchanged within severalmonths even on storage in light.

The salt H<sub>2</sub>L·2HBr undergoes an irreversible solvolytic dissociation up to the free base in diluted ( $c <5 \times 10^{-5}$  M) DMF solutions.

 $H_2L \cdot 2HBr_{Solv} + 2B_{Solv} \rightarrow H_2L_{Solv} + 2[B \cdot HBr]_{Solv}$ 

Here B is an electron-donor solvent.

Unlike such ligands as alkyl-substituted 3,3'-bis-(dipyrrolylmethenes) studied earlier [1, 2], solvolytic dissociation of the salt in DMSO and pyridine solutions ( $c < 5 \times 10^{-5}$  M) proceeds partially. The equilibrium between protonated and molecular forms of the ligand is established in solutions, which is proved by the presence of corresponding bands in the regions of 498–504 and 455–460 nm. Comparison of the positions of the maxima of an intensive band in the spectra of the salt and the molecular ligand points to an increase in the auxochromic proton effect ( $\Delta\lambda_{max} = \lambda_{max}^{salt} - \lambda_{max}^{ligand}$ ) up to 50 nm (see Fig. 1b) as compared with bis(2,4,7,8,9-pentamethyldipyrrolylmethene-3-yl) methane [2], for which the value  $\Delta\lambda_{max}$  does not exceed 40 nm.

According to the regularities [2] found earlier, the revealed distinctions in spectral properties point to a small decrease in the basicity of the ligand 3,3'-bis-(dipyrrolylmethene) upon insertion of the methoxyphenyl group in the 3,3'-spacer, which, obviously, is caused by a domination of the negative induction effect of the substituent over the positive mesomeric effect in the composition of the synthesized ligand

## **EXPERIMENTAL**

Electron absorption spectra in organic solvents were recorded in the range of 300–700 nm on an SF-103 spectrophotometer ("Akvilon," Russia) driven by the Spectr 1.0 program complex. The experiments were carried out in quartz cells with absorbing layer thickness of 1 and 10 mm at a concentration  $10^{-6}$ – $10^{-4}$  M of the solutions under study. Temperature (298.15 K) of solution in the cell was maintained by means of Peltier cell accurate to ±0.1°C. The IR spectra of the dihydrobromide in KBr tablets were taken on an Avatar 360 FT–IR ESP device. The <sup>1</sup>H NMR spectra in deuterated chloroform were recorded on a Bruker 500 NMR spectrometer. Organic solvents (chemicallypure grade) were additionally purified according to the known procedures [4]. According to the results of titration by Fisher's method, water contents in solvents did not exceed 0.02%.

**Bis(2,4-dimethyl-5-ethoxycarbonylpyrrole-3-yl)-**(4'-methoxyphenyl)methane (I). A solution of 5.0 g of 2,4-dimethyl-5-ethoxycarbonylpyrrole, 2 ml of anisic aldehyde, and 4 ml of hydrobromic acid in 50 ml of methanol was boiled within 2 h. Then the solution was cooled, the precipitate was filtered off, washed out with methanol, and dried up in air at room temperature. Yield 6.7 g (98.7%), mp 195–197°C. <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 9.04 s (2H, NH), 7.04 d (2H, CH<sub>Ar</sub>), 6.83 d (2H, CH<sub>Ar</sub>), 5.32 s (1H, *ms*-CH), 4.29 q (4H, OC<u>H</u><sub>2</sub>CH<sub>3</sub>), 3.81 s (3H, OCH<sub>3</sub>), 2.08 s (6H, CH<sub>3</sub>), 1.71 s (6H, CH<sub>3</sub>), 1.36 t (6H, OCH<sub>2</sub>C<u>H</u><sub>3</sub>). Found, %: C 68.90; H 7.03; N 6.02. C<sub>26</sub>H<sub>32</sub>N<sub>2</sub>O<sub>5</sub>. Calculated, %: C 69.01; H 7.13; N 6.19.

**Bis(2,4-dimethylpyrrole-3-yl)(4'-methoxyphenyl)methane (II).** A solution of 2.0 g of bis(2,4-dimethyl-5-ethoxycarbonylpyrrole-3-yl)(4'-methoxyphenyl)methane and 2.0 g of potassium hydroxide in 60 ml of ethylene glycol was boiled within 1 h. The mixture was poured out in 200 ml of water, sodium acetate was added, and the precipitate was filtered off, washed out with water, and dried up in air at room temperature. Yield 1.3 g (99%). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 7.42 s (2H, NH), 7.02 d (2H, CH<sub>Ar</sub>), 6.88 d (2H, CH<sub>Ar</sub>), 5.38 s (1H, *ms*-H), 3.84 s (3H, OCH<sub>3</sub>), 1.78 s (6H, 4,4'-CH<sub>3</sub>), 1.70 s (6H, 2,2'-CH<sub>3</sub>). Found, %: C 77.61; H 7.21; N 8.87. C<sub>20</sub>H<sub>24</sub>N<sub>2</sub>O. Calculated, %: C 77.89; H 7.84; N 9.08.

Bis(2,4,7,8,9-pentamethyldipyrrolylmethene-3-yl)(4'-methoxyphenyl)methane dihydrobromide (III).

To a solution of 1.4 g of bis(2,4-dimethylpyrrole-3-yl)-(4'-methoxyphenyl)methane and 1.3 g of 2-formyl-3.4.5-trimethylpyrrole in 50 ml of methanol 1.5 ml of hydrobromic acid was added. The precipitate was filtered off, washed out with methanol, and dried up in air at room temperature. Yield 3.2 g (98%). Electronic absorption spectrum,  $\lambda_{max}$ , nm (log  $\epsilon$ ): 374–396 (4.00) ctb, 465 (4.72) sh, 504 (4.97) (DMF,  $c \sim 1 \times 10^{-4}$  M), 454 (4.71) (DMF,  $c \sim 1 \times 10^{-6}$  M); 364 (4.03) ctb, 465 (4.82), 505 (5.20) (CHCl<sub>3</sub>); 374 (4.02) ctb, 467 (4.81), 507 (5.17) (C<sub>6</sub>H<sub>6</sub>). IR spectrum,  $v_{NH}$  3454 cm<sup>-1</sup>. <sup>1</sup>H NMR spectrum, δ, ppm: 13.19 s (2H, NH), 12.98 s (2H, NH), 7.06 s (2H, ms-H), 6.96 d (2H, H-Ph), 6.87 d (2H, H-Ph), 5.37 s (1H, ms-H), 3.82 s (3H, OCH<sub>3</sub>), 2.68 s (6H, CH<sub>3</sub>), 2.30 s (6H, CH<sub>3</sub>), 2.26 s (6H, CH<sub>3</sub>), 2.00 s (6H, CH<sub>3</sub>), 1.98 s (6H, CH<sub>3</sub>). Found, %: C 60.92; H 6.17; N 7.87. C<sub>36</sub>H<sub>44</sub>N<sub>4</sub>OBr<sub>2</sub>. Calculated, %: C 61.02; H 6.26; N 7.91.

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